PATENT ABSTRACTS OF JAPAN

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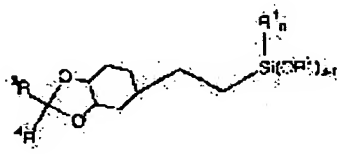
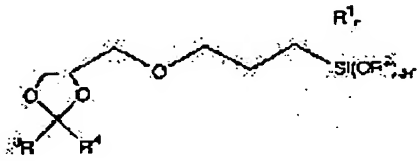
(54) NEW SILANE COUPLING AGENT

(57)Abstract:
PROBLEM TO BE SOLVED: To obtain a new compound comprising a specific compound having a 1,3-dioxolane ring and an alkoxysilyl group in one molecule and useful as a silane coupling agent utilizable as an additive for adhesives, sealants and primers.
SOLUTION: This new compound is represented by formula I [R1 and R2 are each methyl or ethyl; R3 and R4 are each H or a 1-6C hydrocarbon or R3 and R4 may each be a cyclically bonded group; (n) is an integer of 0-2] or formula II, etc., and has 1,3-dioxolane ring and an alkoxysilyl group and useful as a silane coupling agent, etc., utilized as an additive, etc., for adhesives, sealant and primers. The compound is obtained by reacting an epoxy group- containing alkoxysilane compound with a ketone or an aldehyde in the presence of an acid catalyst or reacting an alkenyl group-containing epoxy compound with a ketone to synthesize a dioxolane ring and reacting the resultant product with an Si-H group-containing alkoxysilane compound.



I



II

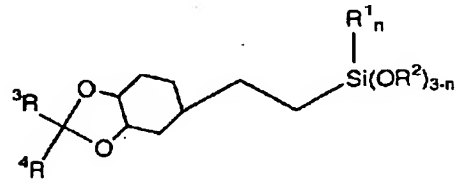
III

LEGAL STATUS

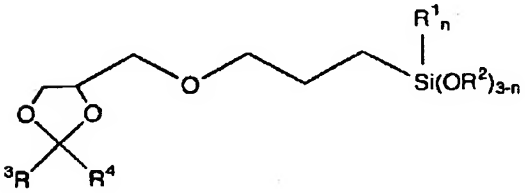
[Date of request for examination]	02.12.2002
[Date of sending the examiner's decision of rejection]	
[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]	
[Date of final disposal for application]	
[Patent number]	3819087
[Date of registration]	23.06.2006
[Number of appeal against examiner's decision of rejection]	
[Date of requesting appeal against examiner's decision of rejection]	
[Date of extinction of right]	

CLAIMS

[Claim(s)]
[Claim 1] The compound which has 1 and 3-dioxolane ring and an alkoxy silyl radical in 1 molecule.
[Claim 2] The compound according to claim 1 whose compound which has 1 and 3-dioxolane ring and an alkoxy silyl radical in 1 molecule is a compound expressed with the following type (1) or (2).
[Formula 1]



(1)



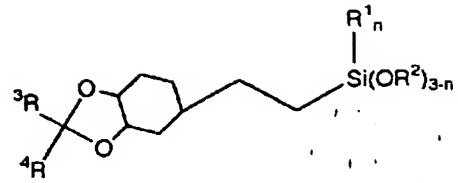
(2)

(Even if R1 and R2 are the same, they may differ from each other, and they are a methyl group or an ethyl group independently, respectively.) R3 and R4 You may differ, even if the same, and it is a hydrogen radical or the hydrocarbon group of carbon numbers 1-6 independently, respectively, or is R3 and R4. You may be the radical combined annularly. n is the integer of 0-2.

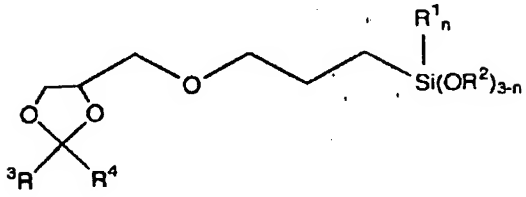
[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the new molecular entity which has 1 and 3-dioxolane ring and an alkoxy silyl radical. It is related with the new molecular entity which has 1 [useful as a silane coupling agent used as an additive of adhesives a sealant, and a primer in detail], 3-dioxolane ring, and an alkoxy silyl radical.
[0002]
[Description of the Prior Art] Conventionally, various silane coupling agents are used for the adhesive manifestation. Also in it, the epoxy group content silane coupling agent is broadly used as an additive of adhesives, a sealant, and a primer. However, under the tertiary amine compound existence too used as additives, such as adhesives, in order that an epoxy group may carry out the polymerization of the glycidyl ether type epoxy group content silane coupling agent, it has the trouble of being inferior to storage stability. Moreover, an alicyclic epoxy group content silane coupling agent has the trouble of the range which an adhesive property can use low being limited.
[0003]
[Problem(s) to be Solved by the Invention] The object is excellent in storage stability irrespective of the class of additive which lives together by this invention reviewing and constituting the trouble which the above-mentioned conventional technique has, and it excels also in an adhesive property, and is going to provide a broad application with a new molecular entity useful as an usable silane coupling agent.
[0004]
[Means for Solving the Problem] This invention offers the compound which has 1 and 3-dioxolane ring and an alkoxy silyl radical in 1 molecule.
[0005] Moreover, it is desirable that the compound which has 1 and 3-dioxolane ring and an alkoxy silyl radical in said 1 molecule is a compound expressed with the following type (1) or (2).
[Formula 2]



(1)



(2)

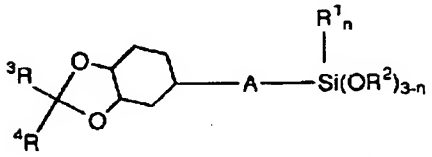
(Even if R1 and R2 are the same, they may differ from each other, and they are a methyl group or an ethyl group independently, respectively.) R3 and R4 You may differ, even if the same, and it is a hydrogen radical or the hydrocarbon group of carbon numbers 1-6 independently, respectively, or is R3 and R4. You may be the radical combined annularly. n is the integer of 0-2.

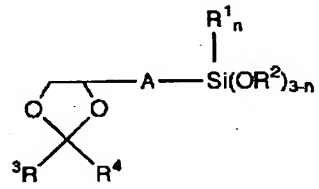
[0006]

[Embodiment of the Invention] Hereafter, this invention is further explained to a detail. Especially definition will not be carried out if the new molecular entity of this invention is the structure of having respectively 1 and 3-dioxolane ring and one or more alkoxy silyl radicals in 1 molecule. For example, it is expressed with the following general formula.

[0007]

[Formula 3]



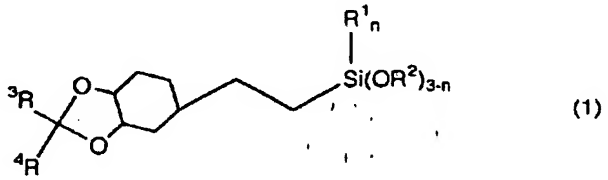


[0008] Among the above-mentioned formula, A may be a divalent hydrocarbon group, for example, a divalent aliphatic series radical, divalent aromatic series radicals, or such combination, and, in addition to carbon and hydrogen, may also contain other atoms, for example, an oxygen atom, a sulfur atom, a nitrogen atom, etc. as a desirable example of A, the alkylene group of carbon numbers 2-6, for example, ethylene, and the alkylene ether group of the 3-methyl-pentyl radical; carbon numbers 4-8, for example, the hydrocarbon ester group of the methylpropyl ether group; carbon numbers 5-10 etc., are mentioned.

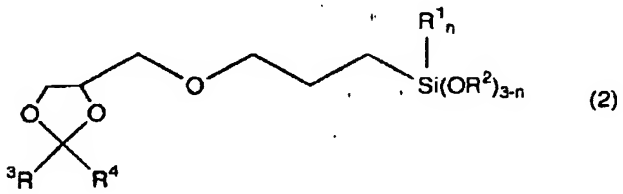
[0009] As a desirable mode of the new molecular entity of above-mentioned this invention, the compound shown by the following formula (1) and (2) can be shown.

[0010]

[Formula 4]

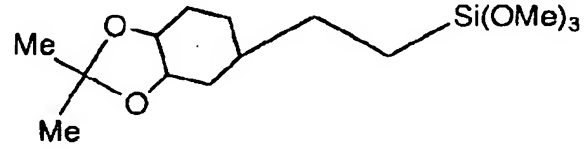


(1)

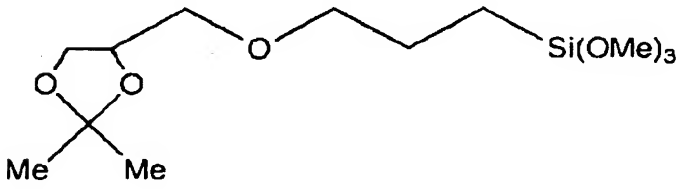


(2)

[0011] It is R1 and R2 here. You may differ, even if the same, and they are a methyl group or an ethyl group independently, respectively. n is 0, 1, or 2 and is 0 or 1 preferably. R3 and R4 You may differ, even if the same, and they are a hydrogen radical or the hydrocarbon group of carbon numbers 1-6 independently, respectively. Aryl groups of the; carbon numbers 6-12, such as the alkyl group which specifically has the shape of a straight chain and branched chain of carbon numbers 1-6, for example, a methyl group, an ethyl group, and n-propyl group, for example, a phenyl group etc.,; it is the cycloalkyl radical of carbon numbers 4-7, R3 [for example,]. R4 A cyclopentylic group, a cyclohexyl radical, etc. to combine are mentioned.
[0012] As a desirable example of a compound expressed with the above-mentioned formula (1) and (2), the compound expressed with the following type (3) and (4) about each of the above-mentioned formula (1) and (2) can be shown.
[0013]
[Formula 5]



(3)



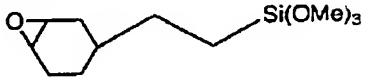
(4)

[0014] The new molecular entity which has 1 and 3-dioxolane ring and an alkoxy silyl radical in 1 molecule of this invention is compoundable by the following two approaches.
Approach 1: Make an epoxy group content alkoxysilane compound, a ketone, or an aldehyde react to the bottom of acid-catalyst existence.
Approach 2: Make the alkoxysilane compound containing a Si-H radical react after making an alkenyl radical content epoxy compound and a ketone react and compounding a dioxolane ring.
[0015] As an epoxy group content alkoxysilane compound in an approach 1, the compound which has respectively ring type aliphatic series epoxy groups, such as an ethylene oxide radical, and a tricyclo decene oxide radical, a cyclopentene oxide radical, a cyclohexene-oxide radical,

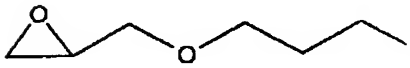
and one or more alkoxysilane radicals can be used. Moreover, an alkoxysilane radical content epoxy resin can also be used. Commercial items, such as an epoxy group content alkoxysilane compound shown by (the compound which has respectively an ethylene oxide radical, an alkoxysilane radical and a cyclohexene-oxide radical, and an alkoxysilane radical at the molecule end, for example, the following type, (5), and 6), can be respectively used for composition of the new molecular entity of this invention especially shown by said formula (1) and (2) suitably.

[0016]

[Formula 6]



(5)



(6)

[0017] Moreover, as a ketone in an approach 1, acetone, 2-butanone, 2-pentanone, 3-methyl-2-butanone, 3-pentanone, 2-hexanone, 4-methyl-2-pentanone, 4-heptanone, 3, and 3-dimethyl-2-butanone, cyclopentanone, a cyclohexanone, etc. are illustrated. Also in this, an acetone and 2-butanone are desirable. As an aldehyde, propionaldehyde, n-butyraldehyde, valeric aldehyde, caproaldehyde, heptaldehyde, a phenyl aldehyde, a benzaldehyde, etc. are illustrated.

[0018] As an acid catalyst, Lewis acid, such as phosphoric acid, a sulfuric acid, and an iron(II) chloride, chlorination tin (IV), a zinc chloride, boron-trifluoride ethyl ether-boron trifluoride, etc. can be used, and Lewis acid can be suitably used also in these.

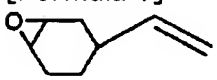
[0019] In an approach 1, although the compound which has 1 and 3-dioxolane ring and an alkoxy silyl radical in 1 molecule of this invention by making the above-mentioned epoxy group content alkoxysilane compound, the above-mentioned ketone, or the above-mentioned aldehyde react to the bottom of existence of the above-mentioned acid catalyst is compoundable, Lewis acid can be used as an acid catalyst as a desirable mode. However, although it becomes a problem at them since the polymerization reaction of the epoxy compound by Lewis acid may occur as side reaction in 1 with the ring opening reaction by the Lewis acid of an epoxy group, and a ketone, and the generation reaction of 3-dioxolane ring An equivalent activity is carried out two to 7 times more preferably. a ketone -- an epoxy group -- desirable -- the 1.5 to 10 time equivalent -- If Lewis acid is added 0.5 to 3% of the weight more preferably 0.05 to 5% of the weight and 40 degrees C or less of reaction temperature are made to react below 30 degrees C more preferably, since a polymerization reaction can be suppressed, it is desirable. However, also in this reaction, since a polymerization reaction may occur, vacuum distillation can be performed and the compound of target this invention can be isolated.

[0020] As said alkenyl radical content epoxy compound used for an approach 2, the compound which has respectively one or more an epoxy group and alkenyl radicals, such as ring type aliphatic series epoxy groups, such as an ethylene oxide radical and a cyclohexene-oxide radical, can be used, and an alkenyl radical content epoxy resin can also be used. Commercial items, such as an alkenyl radical content epoxy compound shown from (the compound which has a cyclohexene-oxide radical and an alkenyl radical, for example, the following formula, (8), and 9), can be respectively used for new molecular entity composition of this invention shown in

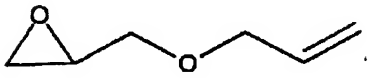
new molecular entity composition of this invention especially shown by said formula (1) by the compound which has an ethylene oxide radical and an alkenyl radical, for example, the following type, (7), and said formula (2) suitably.

[0021]

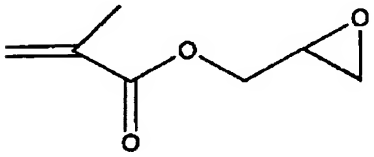
[Formula 7]



(7)



(8)

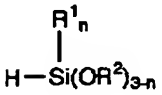


(9)

[0022] The ketone illustrated by the approach 1 can be used for the ketone used in an approach 2. As an alkoxysilane compound containing a Si-H radical, the alkoxysilane compound shown in the following type (10) can be used. The inside of a formula, R1, and R2 R1 in said formula (1) and (2), and R2 It is synonymous.

[0023]

[Formula 8]



(10)

[0024] In an approach 2, the alkenyl radical content 1 and 3-dioxolane compound are compoundable from said alkenyl radical content epoxy compound and said ketone first using a well-known synthetic approach, for example, an approach given in JP,52-95669,A etc. namely, the epoxy group of said alkenyl radical content epoxy compound -- receiving -- 65% phosphoric acid or concentrated sulfuric acid -- equimolar -- further -- said ketone -- 10 - 20 time mol -- it adds. In order to forbid the polymerization reaction of an alkenyl radical through this synthetic reaction, polymerization inhibitor, such as a cupric chloride, is further added 0.05 to 0.1% of the weight to said alkenyl radical content epoxy compound. Thus, by reacting by agitating the obtained mixture at 60 degrees C for 2 hours, ketal-ization is performed between an epoxide ring or a cyclohexene-oxide ring, and a ketone, and 1 and 3-dioxolane ring is compounded. Subsequently, the hydrogen atom which combined the alkoxysilane compound containing said Si-H radical with the alkenyl radical in this dioxolane compound and the silicon of this alkoxysilane compound can compound the compound with which equimolar or an alkoxysilane compound has 1 and 3-dioxolane ring and an alkoxy silyl radical in 1 molecule of this invention by mixing under existence of the catalyst of platinum metal content compounds, such as platinum and a platinic chloride, etc. so that it may become an excess a little. What is necessary is for the addition of the catalyst of platinum etc. just to have sufficient amount to promote the reaction between the above-mentioned dioxolane compound and the above-mentioned alkoxysilane compound, and just to define optimum dose according to the catalyst to be used.

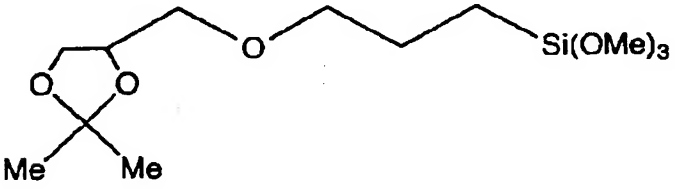
[0025]

[Example] Although this invention is explained still more concretely below, this invention is not restricted to these.

[0026] (Example 1) Acetone 100g and epoxy silane (A-187, Nippon Unicar make) 100g were put into the three necked flask, and it ice-cooled. Subsequently, boron-trifluoride ethyl ether-boron trifluoride (BF3 and OEt2) 2g was melted to the 25g acetone, and it was slowly dropped at the three necked flask. Although reaction temperature rose, it was made not to go up at 30 degrees C or more. It stirred under 1-hour ice-cooling after dropping termination. After acetone distilling off, vacuum distillation was carried out and the compound which has 1 and 3-dioxolane ring and an alkoxy silyl radical in 1 molecule was compounded. The boiling points were 115 degrees C / 0.1mmHg. Yield was 52%. The structure of the obtained compound was checked in NMR. An NMR chart is shown in drawing 1 . A chemical structure type is shown by the following type (11).

[0027]

[Formula 9]

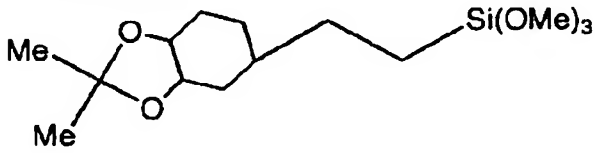


(11)

[0028] (Example 2) Acetone 100g and epoxy silane (A-186, Nippon Unicar make) 100g were put into the three necked flask, and it ice-cooled. Subsequently, boron-trifluoride ethyl ether-boron trifluoride (BF3 and OEt2) 0.2g was melted to the 25g acetone, and it was slowly dropped at the three necked flask. Although reaction temperature rose, it was made not to go up at 30 degrees C or more. It stirred under 1-hour ice-cooling after dropping termination. After acetone distilling off, vacuum distillation was carried out and the compound which has 1 and 3-dioxolane ring and an alkoxy silyl radical in 1 molecule was compounded. The boiling points were 135 degrees C / 0.1mmHg. Yield was 48%. The structure of the obtained compound was checked in NMR. An NMR chart is shown in drawing 2 . A chemical structure type is shown by the following type (12).

[0029]

[Formula 10]



(12)

[0030]

[Effect of the Invention] carrying out a polymerization also under tertiary amine compound existence, since the new molecular entity of this invention does not have a glycidyl ether type epoxy group in intramolecular -- there is nothing -- storage Nakayasu -- it is a law. Moreover, like an alicyclic epoxy group content silane coupling agent, since the adhesive property is low, an application is not limited. For this reason, also under tertiary amine compound existence, the new molecular entity of this invention is stable, and useful as a silane coupling agent usable for broad applications, such as an additive of a primer, a sealant, and adhesives.

[Translation done.]

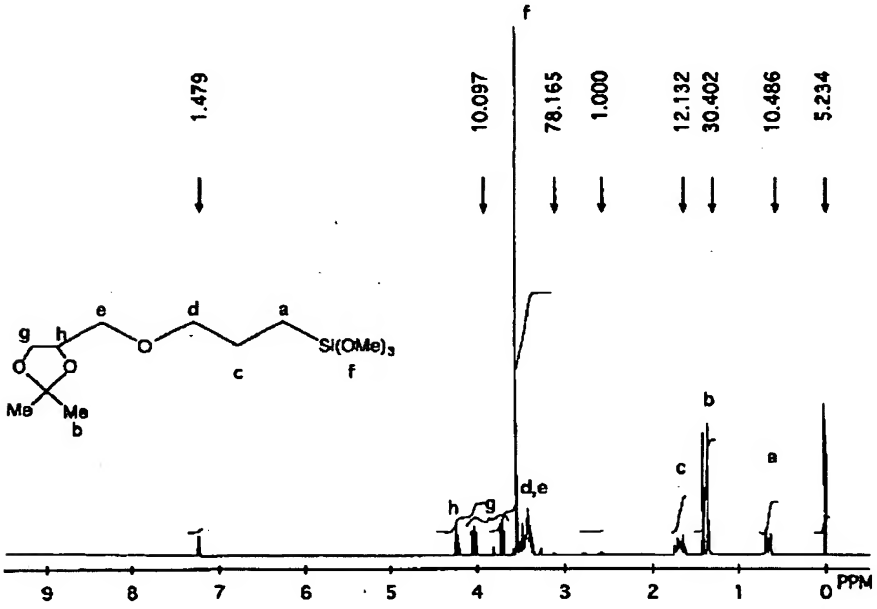
DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is drawing showing the NMR chart of the compound which has 1 and 3-dioxolane ring and an alkoxy silyl radical in 1 molecule expressed with a formula (11).
[Drawing 2] It is drawing showing the NMR chart of the compound which has 1 and 3-dioxolane ring and an alkoxy silyl radical in 1 molecule expressed with a formula (12).

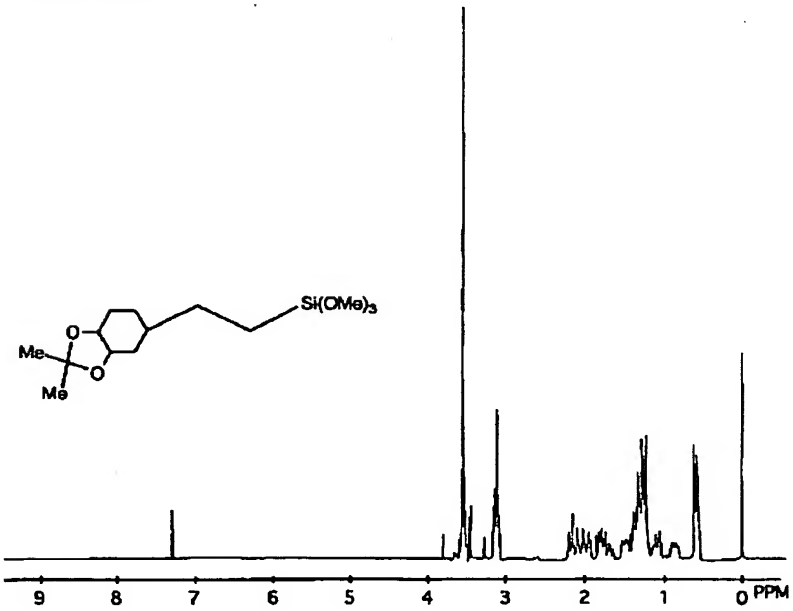
[Translation done.]

DRAWINGS

[Drawing 1]



[Drawing 2]



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